



Solvent extraction of nickel and cobalt with synergistic systems consisting of carboxylic acid and aliphatic hydroxyoxime

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Abstract

Metal extraction pH isotherms and extraction and stripping kinetics have been determined with Versatic 10 acid and LIX® 63 and modifier TBP in an attempt to develop synergistic SX systems for the separation, purification and recovery of nickel and cobalt from leach solutions.

The combination of LIX® 63 with Versatic 10 acid resulted in significant synergistic shifts for nickel, cobalt, copper, zinc, and manganese and antagonistic shifts for calcium and magnesium. With the 0.5 M Versatic 10 acid/0.35 M LIX® 63 system, the ΔpH_{50} values of nickel, cobalt, copper, zinc and manganese compared to Versatic 10 acid alone were found to be 2.79, 3.50, >2.0, 1.99 and 1.17 pH units, respectively. The $\Delta\text{pH}_{50(\text{Mn-Ni})}$ and $\Delta\text{pH}_{50(\text{Mn-Co})}$ values were found to be 1.96 pH and 2.53 pH units, respectively, indicating easy separation of nickel and cobalt from manganese, calcium and magnesium. The extraction and stripping kinetics of cobalt, copper, zinc, and manganese were fast and the extraction and stripping kinetics of nickel were slow with the Versatic 10 acid/LIX® 63 synergistic system. The nickel stripping kinetics increased with the addition of TBP. Within 2 min, the stripping efficiency of nickel increased from 18% with no TBP to 91% with 0.5 M TBP addition. The addition of TBP to the Versatic 10 acid/LIX® 63 system also improved the nickel extraction kinetics.

It is proposed that in the Versatic 10 acid/LIX® 63 synergistic system, LIX® 63 plays the role of an extractant and Versatic 10 acid a synergist for nickel while LIX® 63 plays the role of a synergist and Versatic 10 acid an extractant for cobalt.

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1. Introduction

LIX® 63, an aliphatic α -hydroxyoxime with the active component 5,8-diethyl-7-hydroxydodecan-6-one oxime (Swanson, 1965), has been the favoured synergist in solvent extraction (SX) research on the recovery of copper, nickel and cobalt from the 1960s. The synergism of organic systems involving LIX® 63 and a number of carboxylic acids has been studied. The synergistic effect of

LIX® 63/naphthenic acid system on the extraction of copper and cobalt was investigated by Flett and Titmuss (1968). Remarkable synergism was observed for both copper and cobalt. By adding 0.1 M naphthenic acid to a 10% LIX® 63-kerosene solution, the pH_{50} of Cu in a nitrate solution shifted from 2.50 with 10% LIX® 63 alone to 1.79 pH units, indicating a ΔpH_{50} of 0.71 pH units. Similarly, the pH_{50} of Co shifted from 5.65 with 10% LIX® 63 alone to 3.02 pH units, indicating a ΔpH_{50} of 2.63 pH units.

The extraction of nickel with α -hydroxy oxime/carboxylic acid mixtures was of considerable potential

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commercial interest in the 1960s and 1970s due to the fact that separation factors of up to 50 were observed for nickel over cobalt in sulphate solutions and the ability to extract nickel in preference to ferric ion, which was then unmatched by any existing commercial SX reagents or reagent combinations (Flett et al., 1974). However, the nickel extraction kinetics with the α -hydroxy oxime/carboxylic acid systems were very slow, taking about 3 h to reach equilibrium at room temperature. This was in contrast to the quick kinetics with the individual reagents (either α -hydroxy oxime or carboxylic acids) with 10 min being the maximum equilibrium time. It was observed that the interfacial tension of lauric acid in hexane–aqueous solution dropped much more with an aqueous solution containing nickel than with copper and cobalt. This corresponded with the slow extraction kinetics for nickel and fast kinetics for copper and cobalt in the α -hydroxy oxime/carboxylic acid mixtures. Therefore, Flett et al. (1974) attributed the slow nickel extraction kinetics to the interfacial effect in the system. It seems that the key to the well-known slow nickel extraction kinetics by LIX® 63 is to monitor the interfacial effects. It was found that the stoichiometry of the mixed complex formed on the extraction of nickel with the α -hydroxy oxime/lauric acid system is $\text{Ni}(\text{O}_x)_2(\text{RH})_2$, where O_x is the de-protonated α -hydroxy oxime (HO_x) and RH lauric acid.

Much research has been carried out to separate nickel and cobalt from other metals using synergistic SX systems (Preston and du Preez, 1994, 2000; du Preez and Preston, 2004). Cheng and Houchin (2001) used the Versatic 10 acid/decyl-4-pyridinecarboxylate ester synergistic system to separate nickel and cobalt from the main impurities, manganese, magnesium, and calcium, and developed novel processes to directly recover nickel and cobalt from leach solutions without intermediate precipitation and re-leach. This system was successfully tested in batch and semi-continuous modes using pilot plant laterite leach solutions (Cheng, 2003; Cheng and Urbani, 2003; Cheng et al., 2003, 2004). An almost complete separation of nickel, cobalt, copper, and zinc from manganese, magnesium, calcium and chloride was achieved. However, the synergist, decyl-4-pyridinecarboxylate ester, is not commercially available, which makes it difficult to commercialise the novel process in the nickel industry.

Efforts were made to use commercially available reagents for the development of synergistic systems to separate Ni and Co from Mn, Mg and Ca using Versatic 10 acid and LIX® 63, which resulted in the development of novel SX processes (Cheng and Urbani, 2005a,b). This paper summarises the development of these synergistic systems.

2. Experimental

... The synthetic solution, simulating a laterite leach solution after iron precipitation and containing 3 g/L Ni, 0.3 g/L Co, 0.2 g/L Cu and Zn, 2.0 g/L Mn, 10.0 g/L Mg and 0.5 g/L Ca, was made by dissolving the required amount of analytical grade metal sulphates in distilled water. Industrial grade Versatic 10 acid was supplied by Shell Chemicals, Australia and LIX® 63 containing 70% of the active component was supplied by Cognis, Australia. TBP (tri-butyl phosphate) was purchased from Sigma-Aldrich. The reagents were diluted in Shellsol 2046, also supplied by Shell Chemicals, Australia.

For the determination of extraction pH isotherms, fresh organic and the synthetic leach solutions were mixed at an A:O ratio of 1:1 and 40 °C. After mixing for 5–10 min when the pH was stable at each target pH point, samples were collected at 0.5 pH intervals.

For the determination of extraction kinetics, an ideal extraction pH for each system was determined from the pH isotherms. A preliminary extraction test was conducted with an A/O ratio of 1:1 at 40 °C and the selected pH to determine the amount of ammonia solution required for pre-equilibration. The organic solution was pre-equilibrated with the pre-determined amount of ammonia solution. The synthetic laterite leach solution and the pre-equilibrated organic solution were mixed at an A/O ratio of 1:1 and 40 °C. Samples of the solution mixture were taken at 0.5, 1.0, 1.5, 2.0, 3.0, 5.0 and 10 min.

For the determination of stripping kinetics, a loaded organic solution was prepared by the extraction of metals from the synthetic laterite leach solution at an A:O ratio of 1:1 and 40 °C with an ideal extraction pH. The loaded organic solution was mixed with the strip solution at an A/O ratio of 1:1 and at 40 °C. Samples of the solution mixture were taken at 0.5, 1.0, 1.5, 2.0, 3.0 and 5.0 min.

The organic and aqueous phases of the collected samples were separated using separating funnels. The organic samples were stripped with 100 g/L sulphuric acid and all aqueous samples were analysed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

3. Results and discussion

3.1. Versatic 10 acid/LIX® 63 system

3.1.1. Extraction pH isotherms with Versatic 10 acid/LIX® 63 system

Metal extraction pH isotherms were determined using the synthetic laterite leach solution and organic solutions containing 0.5 M Versatic 10 acid alone (Fig. 1) and 0.5 M LIX® 63 alone (Fig. 2), 0.5 M Versatic 10 acid and 0.1 M,

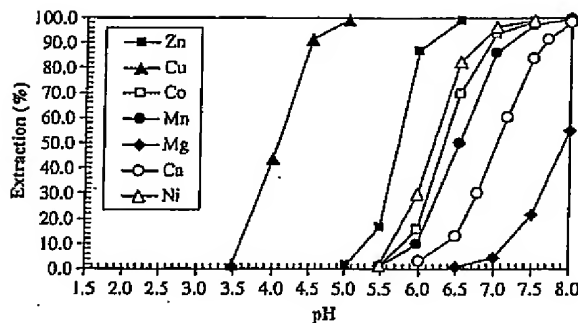


Fig. 1. Extraction pH isotherms of metals with 0.5 M Versatic 10 acid in Shellsol 2046 and the synthetic laterite leach solution at an A:O ratio of 1:1 and 40 °C.

0.2 M, 0.35 M and 0.5 M LIX® 63. The pH_{50} values (the pH value at 50% metal extraction) and ΔpH_{50} values (difference in pH_{50} value with and without LIX® 63) of the metals are shown in Table 1. The addition of LIX® 63 to Versatic 10 acid resulted in significant synergistic shifts for copper with all systems. The synergistic shift for nickel was significant when the concentration of LIX® 63 was 0.2 M or greater, and the synergistic shift for cobalt was significant when the concentration of LIX® 63 was 0.30 M or greater.

The metal pH_{50} values varied with the change in LIX® 63 concentrations. With the addition of 0.1 M LIX® 63, the copper pH isotherm shifted over 2.0 pH units, but the shift of nickel (ΔpH_{50}) was only 0.28 pH units. The cobalt ΔpH_{50} value was only 0.01 pH units (Table 1). With the addition of 0.2 M LIX® 63, the nickel ΔpH_{50} increased considerably to 1.78 pH units, but the cobalt ΔpH_{50} value was only 0.17 pH units. With the addition of 0.3 M LIX® 63, the nickel ΔpH_{50} increased further to 2.84 pH units whilst the cobalt pH isotherm showed a large shift towards lower pH with a ΔpH_{50} of 2.38 pH units. With the addition of 0.35 M LIX® 63 (Table 1 and Fig. 3), the nickel pH isotherm remained unchanged, but cobalt continued to change dramatically to a ΔpH_{50} of 3.50 pH units. The pH isotherms of zinc and manganese also significantly shifted towards lower pH with ΔpH_{50} of zinc and manganese being 1.99 and 1.11 pH units (Table 1), respectively. The further increase in LIX® 63 concentration from 0.35 M to 0.5 M did not affect the metal pH isotherms. Antagonistic shifts for calcium were observed for all systems tested. Some antagonistic shifts were observed for magnesium. This was judged by the lower magnesium extraction at pH 7.5 when LIX® 63 was added (Figs. 1 and 3), although no pH_{50} values for magnesium could be obtained with the synergistic systems.

It is very interesting to note that the shape of the nickel and cobalt isotherms varied with the change in LIX® 63

concentrations. The cobalt pH isotherms changed at low pH when the LIX® 63 concentration was <0.2 M (Fig. 4). With the addition of 0.3 M LIX® 63, the cobalt pH isotherm shifted dramatically towards low pH and showed an unusual "transition shape". When the LIX® 63 concentration was >0.35 M, the cobalt pH isotherm returned to its normal shape. The same trend applied to the nickel pH isotherms (Fig. 5). However, the unusual "transition shape" occurred at a lower LIX® 63 concentration (0.2 M) than for cobalt.

The metal extraction sequence was found to be $Cu > Ni > Co > Zn > Mn$ in the Versatic 10 acid/LIX® 63 system when the LIX® concentration was lower than 0.3 M. It was also noted that with the 0.5 M Versatic 10 acid/0.35 M LIX® 63 system, the cobalt pH isotherm was located lower than that of nickel and the metal extraction order changed to $Cu > Co > Ni > Zn > Mn$. This may imply two different extraction mechanisms. Copper and nickel were extracted by LIX® 63 to form a chelating complex with the carboxylic acid as a solvating reagent (synergist) as reported by Cox and Flett (1971) and Flett et al. (1974). When the concentration of LIX® 63 was low, (0.1 M), copper has the strongest affinity with LIX® 63 and was extracted first, resulting in a large copper pH isotherm shift of over 2.0 pH units. Some nickel was extracted by the same reaction at low pH. The remaining nickel, and all cobalt and zinc were extracted by Versatic 10 acid. This was evident because the pH isotherms of these metals at high pH range did not change. When the LIX® 63 concentration was further increased to 0.2 M, more nickel was extracted by the chelating reaction with LIX® 63 and the solvating reaction with Versatic 10 acid. When the LIX® 63 concentration reached a critical point, all the nickel was extracted by LIX® 63 and Versatic 10 acid. Cobalt, zinc and manganese reacted with Versatic 10 acid to form metal-organic complexes by cation exchange. When extra LIX® 63 was available (>0.3 M), further reaction occurred to form cobalt-, zinc- and manganese-

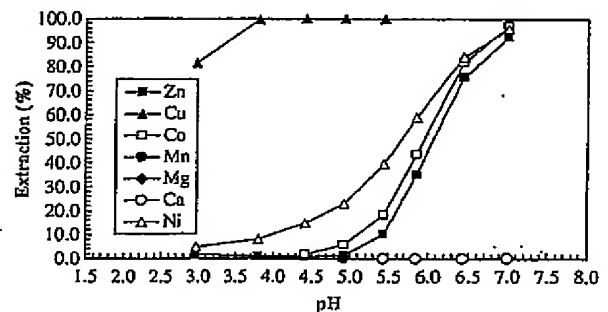


Fig. 2. Extraction pH isotherms of metals with 0.5 M LIX® 63 in Shellsol 2046 and the synthetic laterite leach solution at an A:O ratio of 1:1 and 40 °C.

Table 1
pH₅₀ and ΔpH₅₀ values of metals with Versatic 10 acid, Versatic 10 acid/LIX® 63 and Versatic 10 acid/LIX® 63/TBP systems

0.5 M Versatic 10 acid	Metals							
	pH	Ni	Co	Cu	Zn	Mn	Mg	Ca
+No synergist	pH ₅₀	6.19	6.33	4.07	5.72	6.53	7.93	7.03
+0.1 M LIX® 63	pH ₅₀	5.91	6.32	<2.0*	5.35	6.79	NA	7.67
	ΔpH ₅₀	0.28	0.01	>2.0*	0.37	-0.26	NA	-0.64
+0.2 M LIX® 63	pH ₅₀	4.41	6.16	<2.0*	5.30	6.80	NA	7.53
	ΔpH ₅₀	1.78	0.17	>2.0*	0.42	-0.27	NA	-0.50
+0.3 M LIX® 63	pH ₅₀	3.35	3.95	<2.0*	4.90	6.65	NA	7.56
	ΔpH ₅₀	2.84	2.38	>2.0*	0.82	-0.12	NA	-0.53
+0.35 M LIX® 63	pH ₅₀	3.40	2.83	<2.0*	3.73	5.36	NA	7.25
	ΔpH ₅₀	2.79	3.50	>2.0*	1.99	1.17	NA	-0.22
+0.5 M LIX® 63	pH ₅₀	3.48	2.88	<2.0*	3.77	5.42	NA	7.44
	ΔpH ₅₀	2.71	3.45	>2.0*	1.95	1.11	NA	-0.41
+0.35 M LIX® 63 & 0.5 M TBP	pH ₅₀	4.01	4.52	<2.0*	5.10	6.63	NA	>7.5*
	ΔpH ₅₀	2.18	1.81	>2.0*	0.62	0.90	NA	-0.47*

* Estimated, NA = not available.

Versatic10-LIX® 63 complexes, where LIX® 63 acted as a solvating reagent (synergist) and the pH isotherms of cobalt, zinc and manganese shifted to lower pH.

The ΔpH_{50(Mn-Ni)} and ΔpH_{50(Mn-Co)} values for the synergistic systems are shown in Table 2. The ΔpH_{50(Mn-Ni)} values for the systems containing over 0.2 M LIX® 63 are in the range of 1.94–3.3 pH-units, indicating easy separation of nickel from manganese. However, the separation of nickel and cobalt from manganese would be difficult using the systems containing 0.1 M and 0.2 M LIX® 63 as the ΔpH_{50(Mn-Co)} values are small (0.47 and 0.64 pH units, respectively). The ΔpH_{50(Mn-Co)} value increased significantly to 2.70 pH units when the concentration of LIX® 63 increased to 0.3 M, indicating that nickel and cobalt can be easily separated from manganese by extraction using the 0.5 M Versatic 10 acid/0.3 M LIX® 63 system. The ΔpH_{50(Mn-Ni)} and ΔpH_{50(Mn-Co)} values dropped when the LIX® 63 concentration was increased to 0.35 M due to the large synergistic shift of manganese (Table 1). A further

increase in LIX® 63 concentration to 0.5 M saw no significant change in ΔpH_{50(Mn-Ni)} and ΔpH_{50(Mn-Co)} values.

In terms of selectivity of nickel and cobalt over manganese (ΔpH_{50(Mn-Ni)} and ΔpH_{50(Mn-Co)} values), the current system is much better than the synergistic systems previously reported. These include the Versatic 10 acid/2-ethylhexanal oxime (EHO) system (Preston, 1983), the Versatic 10 acid/*n*-octyl-3-pyridine carboxylate and Versatic 10 acid/CLX50 systems (Preston and du Preez, 1994), the Versatic 10 acid/4-(5-nonyl) pyridine system (Preston and du Preez, 2000), the neodecanoic acid/Mintek system (du Preez and Preston, 2004), and the Versatic 10 acid/decyl-4-pyridine carboxylate system (Cheng and Urbani, 2003; Cheng et al., 2004). The ΔpH_{50(Mn-Ni)} and ΔpH_{50(Mn-Co)} values of the current study and those reported previously are listed in Table 3 for comparison. In addition, EHO is not stable and the other synergists are not commercially available.

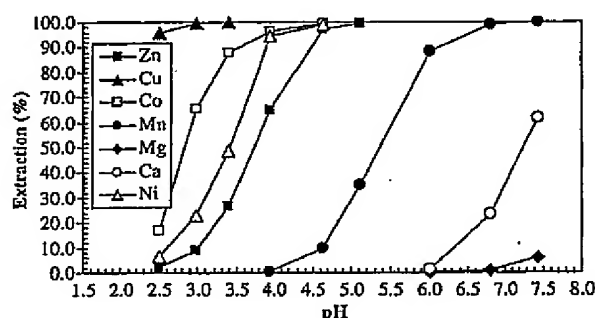


Fig. 3. Extraction pH isotherms of metals with 0.5 M Versatic 10 acid/0.35 M LIX® 63 in Shellisol 2046 and the synthetic laterite leach solution at an A:O ratio of 1:1 and 40 °C.

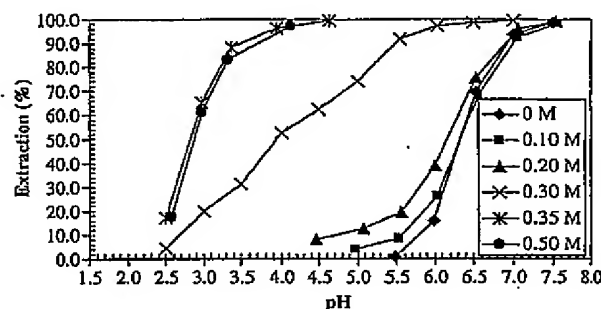


Fig. 4. Effect of LIX® 63 on cobalt extraction with 0.5 M Versatic 10 acid and LIX® 63 in Shellisol 2046 and the synthetic laterite leach solution at 40 °C, A/O ratio 1:1.

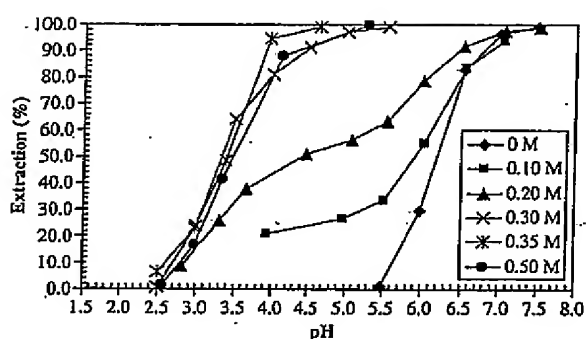


Fig. 5. Effect of LIX® 63 on nickel extraction with 0.5 M Versatic 10 acid and LIX® 63 in Shellsol 2046 and the synthetic laterite leach solution at 40 °C, A/O ratio 1:1.

3.1.2. Extraction kinetics with Versatic 10 acid/LIX® 63 system

The extraction kinetics of nickel, cobalt, copper, zinc and manganese using the 0.5 M Versatic 10 acid/0.35 M LIX® 63 system are shown in Fig. 6. The extraction kinetics of cobalt, copper, zinc and manganese were fast and the extraction kinetics of nickel was relatively slow. Within 30 s, all cobalt and copper and almost all zinc were extracted. However, only 55% Ni was extracted. The extraction efficiency of nickel slowly increased with time and after 10 min reached 86%. The nickel crowded out the cobalt, zinc and manganese, resulting in decreasing extraction efficiencies of these metals with time. The slow extraction kinetics of the LIX® 63–carboxylic acid system was reported by Flett and West (1971) and Flett et al. (1974) although nickel extraction kinetics with the current LIX® 63/Versatic 10 acid system was much faster than that in the systems reported previously. For example, in a LIX® 63/naphthenic acid/kerosene system, about 50% nickel was extracted in 3 h (Flett et al., 1974) compared with 86% nickel extraction in 10 min with the current LIX® 63/Versatic 10 acid/kerosene system. Flett et al. (1974) proposed a correlation between the drop of interfacial tension in the presence of nickel ions and the slow nickel extraction kinetics with the LIX® 63–carboxylic acid system. It would be of interest to find out the cause of the slow nickel extraction kinetics with the synergistic system, given that the nickel extraction ki-

netics with the individual systems was fast (Flett and West, 1971; Cheng and Urbani, 2003).

3.1.3. Stripping kinetics with Versatic 10 acid/LIX® 63 system

The stripping kinetics of nickel, cobalt, copper, zinc and manganese from the loaded 0.5 M Versatic 10 acid/0.35 M LIX® 63 system using a strip solution containing 5 g/L Ni and 10 g/L sulphuric acid at 40 °C are shown in Fig. 7. The stripping kinetics of copper, cobalt, zinc and manganese were fast. Within 30 s, 73% Cu, 80% Co, 95% Zn and 97% Mn were stripped. The stripping efficiency of cobalt increased to 94% within 2 min. The stripping kinetics of nickel was very slow and reached only 18% in 2 min and 32% in 5 min. The slow nickel stripping kinetics is characteristic of the hydroxy oxime–nickel chelating complexes. This further indicated that LIX® 63 acted as an extractant and Versatic 10 acid as a solvating reagent (synergist) for nickel extraction in the current study.

Flett et al. (1974) reported that the mixed complex formed on the extraction of nickel with the α -hydroxy oxime/lauric acid system was $\text{Ni}(\text{O}_x)_2(\text{RH})_2$, where O_x is the de-protonated α -hydroxy oxime (HO_x) and RH the lauric acid. In the current system, a series nickel complexes may form, such as $\text{Ni}(\text{O}_x)_2(\text{RH})_2(\text{H}_2\text{O})_2$, $\text{Ni}(\text{O}_x)_2(\text{RH})_4$, etc. for an octahedral structure with nickel. Further research is needed to determine the dominant nickel complexes, which may change with the concentrations of the organic components. However, LIX® 63 acted as an extractant and Versatic 10 acid acted as a solvating reagent (synergist) for nickel extraction in the current system could be proposed due to its extraction and stripping characteristics of the individual LIX® 63 and Versatic 10 acid systems and their combined system.

3.1.4. Stripping of cobalt from LIX® 63 alone and LIX® 63/Versatic 10 acid systems

Although the above tests showed fast stripping kinetics of cobalt with the Versatic 10 acid/LIX® 63 system, the long-term resistance of the system to cobalt poisoning has not been demonstrated. Preston (1975a,b) reported that the extraction of cobalt(II) by aliphatic α -hydroxyoximes, including 5,8-diethyl-7-hydroxydodecan-6-one oxime,

Table 2

$\Delta\text{pH}_{50(\text{Mn-Ni})}$ and $\Delta\text{pH}_{50(\text{Mn-Co})}$ with the Versatic 10 acid, Versatic 10 acid/LIX® 63 and Versatic 10 acid/LIX® 63/TBP systems

ΔpH_{50} of metals	0.5 M Versatic 10 acid						
	No synergist	0.1 M LIX® 63	0.2 M LIX® 63	0.3 M LIX® 63	0.35 M LIX® 63	0.5 M LIX® 63	0.5 M LIX® 63/TBP
$\Delta\text{pH}_{50(\text{Mn-Ni})}$	0.34	0.88	2.39	3.30	1.96	1.94	2.62
$\Delta\text{pH}_{50(\text{Mn-Co})}$	0.20	0.47	0.64	2.70	2.53	2.54	2.11

Table 3

A comparison of selectivity of nickel and cobalt over manganese for different synergistic systems

Organic systems	$\Delta pH_{50(Mn-Ni)}$	$\Delta pH_{50(Mn-Co)}$	Reference
0.5 M Versatic 10 acid/0.5 M EHO*	2.07	1.22	Preston (1983)
0.5 M Versatic 10 acid/20% v/v CLX50	1.35	0.78	Preston and du Preez (1994)
0.5 M Versatic 10 acid/20% v/v CLX50	1.21	0.68	Cheng and Urbani (2003)
0.5 M Versatic 10 acid/0.5 M <i>n</i> -octyl 3PC*	1.73	1.06	Preston and du Preez (1994)
0.5 M Versatic 10 acid/0.5 M 4-(5-nonyl)pyridine	1.72	1.04	Preston and du Preez (2000)
0.5 M neodecanoic acid/0.5 M Mintek synergist	1.52	0.89	du Preez and Preston (2004)
8% v/v 0.5 M Versatic 10 acid/10% v/v 0.5 M <i>n</i> -decyl 4PC*	1.95	1.17	Cheng and Urbani (2005c)
0.5 M Versatic 10 acid/0.35 M LIX® 63	3.30	2.70	Current study
0.5 M Versatic 10 acid/0.35 M LIX® 63/ 0.5 M TBP	2.62	2.11	Current study

* EHO = 2 ethyl-hexanal oxime, *n*-octyl 3PC = *n*-octyl 3-pyridine carboxylate, *n*-decyl 4PC = *n*-decyl 4-pyridine carboxylate.

the active component of LIX® 63, proceeded irreversibly. However, cobalt(III) is not extracted by these extractants. The complex formed by extraction of cobalt(II) was extremely stable and demonstrated complete inertness towards concentrated acids, indicating the presence of Co(III) rather than Co(II) in the formed complex. However, in the research work conducted by Flett and Titmuss (1968), Flett and West (1971) and Flett et al. (1974), who used synergistic systems of LIX® 63/carboxylic acids including naphthenic acid, Versatic 9–11 acid and α -bromolauric acid to extract cobalt, no difficulties in stripping cobalt or poisoning LIX® 63 by cobalt were reported. This indicates that cobalt may not poison LIX® 63/carboxylic acid systems.

To verify this, parallel tests were conducted with 0.35 M LIX® 63 and the 0.50 Versatic 10 acid/0.35 M LIX® 63 systems to demonstrate the effect of Versatic 10 acid on the stripping of cobalt from LIX® 63. The organic solutions were loaded with an aqueous solution containing 0.5 g/L Co at an A/O ratio of 1:1, 40 °C and pH 7.0 for the LIX® 63 system and pH 5.8 for the LIX® 63/Versatic 10 acid system. All the cobalt was extracted in both systems. The loaded organic solutions were mixed with the raffinate for up to 76 h in containers with air bubbling at

flowrates in the range of 0.3–0.5 L/min. Organic solution samples were taken before mixing, at 26 h and at the end of the tests (76 h). The organic solution samples were stripped with 100 g/L sulphuric acid and the strip liquor was assayed for cobalt (Fig. 8). At the beginning of mixing, only 49% cobalt was stripped from the 0.35 M LIX® 63 system. After mixing for 26 and 76 h with air bubbling, the cobalt stripping efficiency dropped to 43% and 29%, respectively, clearly indicating the poisoning of LIX® 63 hydroxy oxime reagent by cobalt. However, after 76 h of mixing with air bubbling, over 99% cobalt was stripped from the LIX® 63/Versatic 10 acid system.

This cobalt stripping ability, most probably, can be attributed to the different extraction mechanism or different complexes formed in the two organic systems. A chelating/oxidation reaction occurred in the pure LIX® 63 system, forming a very stable Co(III) chelate complex in the presence of oxygen (Preston, 1975a,b). In the current Versatic 10 acid/LIX® 63 system, cation exchange probably occurred with Versatic 10 acid as the extractant and LIX® 63 acted as a solvating reagent to form a cobalt–Versatic 10 acid–LIX® 63 complex. Because no chelating complex was formed in the Versatic 10 acid/LIX® 63 system, cobalt could be easily stripped.

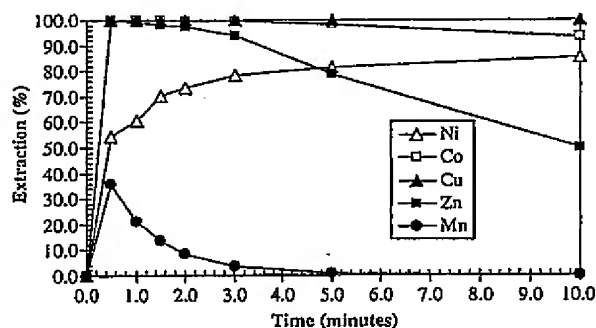


Fig. 6. Extraction kinetics of metals with 0.5 M Versatic 10 acid/0.35 M LIX® 63 in Shellsol 2046 and the synthetic laterite leach solution at an A:O ratio of 1:1 and 40 °C.

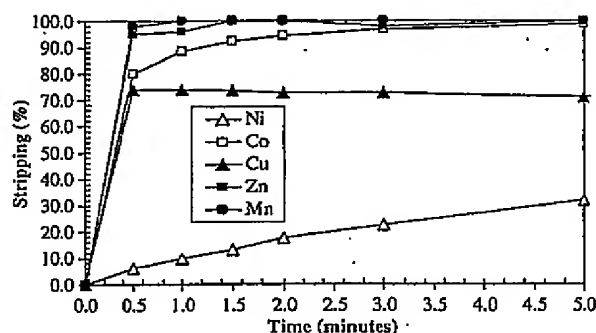


Fig. 7. Stripping kinetics of metals from the loaded 0.5 M Versatic 10 acid/0.35 M LIX® 63 system at an A:O ratio of 1:1 and 40 °C.

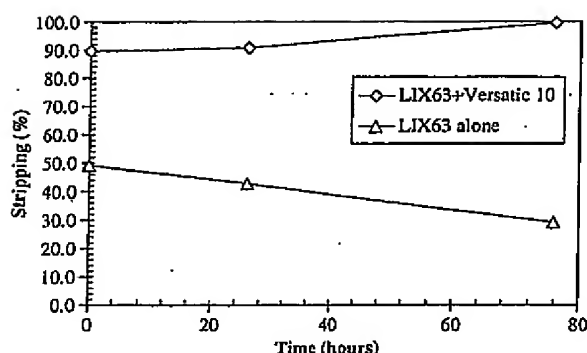


Fig. 8. Stripping efficiency of cobalt from the loaded 0.35 M LIX® 63 and 0.5 M Versatic 10 acid/0.35 M LIX® 63 systems after mixing for up to 76 h with air bubbling.

The relatively low cobalt stripping efficiencies in the 0.5 M Versatic 10 acid/0.35 M LIX® 63 system at the beginning of mixing were probably attributed to the displacement of a small amount of de-protonated LIX® 63 associated with the cobalt by Versatic 10 acid. Once all de-protonated LIX® 63 was displaced, the cobalt stripping efficiency approached 100%.

Preston (1983) reported that the mixed complex formed on the extraction of cobalt with the Versatic 10 acid/EHO system was CoR_2B_4 , where R is the de-protonated Versatic 10 acid and B the EHO molecule. In the current system, a series of cobalt-organic complexes may form, such as $\text{CoR}_2(\text{Ox})_2(\text{H}_2\text{O})_2$, $\text{CoR}_2(\text{Ox})_4$, etc. for an octahedral structure with cobalt. Further research is needed to determine the dominant cobalt/organic complexes, which may change with the concentrations of the organic components. However, that Versatic 10 acid acted as an extractant for cobalt and LIX® 63 acted as a solvating reagent (synergist) for cobalt in the Versatic 10 acid/LIX® 63 system could be proposed due to its stripping characteristics with the individual LIX® 63 and Versatic 10 acid systems and their combined system.

The findings that nickel and cobalt may form different metal/organic complexes in the same organic system are of great interest. In other words, one reagent may act as an extractant for some metals and act as a synergist for others. In the current system, most probably, LIX® 63 acted as an extractant for copper and nickel and a synergist for other metals including cobalt, zinc and manganese while Versatic 10 acid acted as an extractant for cobalt, zinc and manganese and a synergist for copper and nickel.

3.2. Versatic 10 acid/LIX® 63/TBP system

As modifiers have been used in copper solvent extraction to increase the stripping kinetics of LIX® extractants,

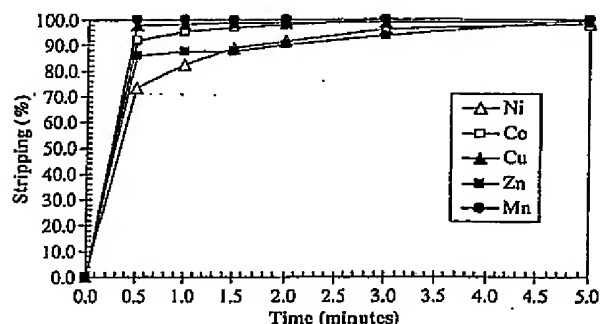


Fig. 9. Stripping kinetics of metals from loaded 0.5 M Versatic 10 acid/0.35 M LIX® 63/0.5 M TBP at an A:O ratio of 1:1 and 40 °C.

modifiers were tried to investigate the possibility of accelerating the nickel stripping kinetics with the Versatic 10 acid/LIX® 63 system. The stripping kinetics tests were conducted using the 0.5 M Versatic 10 acid/0.35 M LIX® 63 system with TBP as a modifier at different concentrations.

3.2.1. Stripping kinetics with the Versatic 10 acid/LIX® 63/TBP system

The stripping kinetics of nickel, cobalt, copper, zinc and manganese from loaded 0.5 M Versatic 10 acid/0.35 M LIX® 63 system with the addition of 0.5 M TBP are shown in Fig. 9. Compared with no addition of TBP (Fig. 7), the nickel stripping kinetics was greatly improved. Within 2 min, the stripping efficiency of nickel increased from 17.7% with no addition of TBP to 91% with 0.5 M TBP addition. As a result, the stripping kinetics of nickel was fast enough for industrial operations. The stripping kinetics of cobalt, copper, zinc and manganese were also very fast. Within 30 s, nearly 100% Mn, 98% Cu, 92% Co and 86% Zn were stripped. In comparison to the 0.5 M Versatic 10 acid/0.35 M LIX® 63

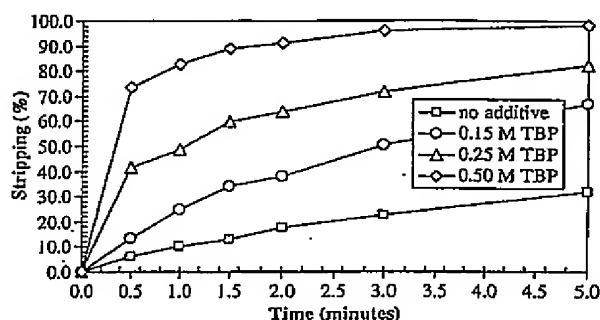


Fig. 10. Effect of TBP concentration on the stripping kinetics of nickel from loaded 0.5 M Versatic 10 acid/0.35 M LIX® 63/TBP at an A:O ratio of 1:1 and 40 °C.

system, the cobalt and copper stripping efficiency also improved considerably. The nickel stripping kinetics increased with increasing TBP concentrations, as shown in Fig. 10.

3.2.2. Extraction pH isotherms with the Versatic 10 acid/LIX® 63/TBP system

While the stripping kinetics of nickel, in particular, increased with the addition of modifier TBP, the effect of the modifier on the pH isotherms and extraction kinetics of the metals with the Versatic 10 acid/LIX® 63 system were unknown. Tests were carried out to determine the effect of TBP using the 0.5 M Versatic 10 acid/0.35 M LIX® 63/0.5 M TBP system. The metal pH isotherms with this system are shown in Fig. 11 and the pH_{50} and ΔpH_{50} values of the metals are also shown in Table 1. Compared with no TBP addition (Fig. 3), the addition of TBP to the Versatic 10 acid/LIX® 63 system resulted in large antagonistic shifts for the metals. The ΔpH_{50} values for nickel, cobalt, zinc and manganese were -0.53 , -1.64 , -1.33 and -1.21 , respectively. The large antagonistic shift for manganese compared to nickel resulted in a larger $\Delta pH_{50(Mn-Ni)}$ value of 2.62 pH units (Table 2) while the larger antagonistic shift for cobalt than manganese resulted in a smaller $\Delta pH_{50(Mn-Co)}$ value of 2.11 pH units. The values of $\Delta pH_{50(Mn-Ni)}$ and $\Delta pH_{50(Mn-Co)}$ were still greater than 2 pH units, indicating that the addition of TBP to the Versatic 10 acid/LIX® 63 system should have no adverse effect on the selectivity of nickel and cobalt over manganese.

3.2.3. Extraction kinetics with the Versatic 10 acid/LIX® 63/TBP system

The extraction kinetics of nickel, cobalt, copper, zinc and manganese with the 0.5 M Versatic 10 acid/0.35 M LIX® 63/0.5 M TBP system are shown in Fig. 12. The extraction kinetics of nickel, cobalt, copper, zinc and manganese was found to be fast. Within 30 s, 83% Ni,

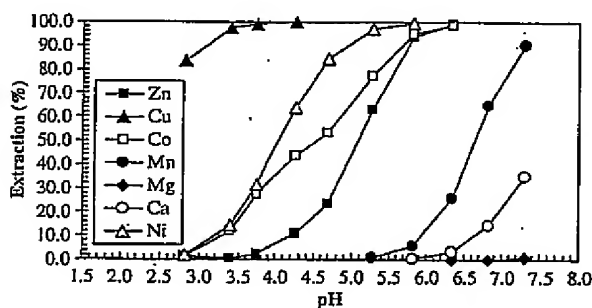


Fig. 11. Extraction pH isotherms of metals with 0.5 M Versatic 10 acid/0.35 M LIX® 63/0.5 M TBP and the synthetic laterite solution at A:O ratio of 1:1, 40 °C.

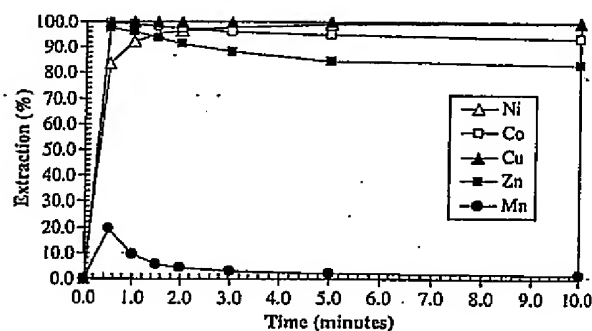


Fig. 12. Extraction kinetics of metals with 0.5 M Versatic 10 acid/0.35 M LIX® 63/0.5 M TBP and the synthetic laterite solution at A:O ratio of 1:1, 40 °C.

over 99% Co, 100% Cu and over 97% Zn were extracted. Some 19% Mn was co-extracted. The manganese extraction dropped significantly with time, due to the crowding out effect by nickel, and after mixing for 2 min, only 4% was extracted compared to over 96% Ni extraction and over 97% Co extraction. The addition of TBP to the Versatic 10 acid/LIX® 63 system not only greatly improved the nickel stripping kinetics, but also greatly improved its extraction kinetics. The mechanism of the increase in nickel extraction and stripping kinetics by the addition of TBP is undergoing further investigation.

4. Conclusions

The combination of LIX® 63 with Versatic 10 acid resulted in significant synergistic shifts for nickel, cobalt, copper, zinc, and manganese and antagonistic shifts for calcium and magnesium. With the 0.5 M Versatic 10 acid/0.35 LIX® 63 system, the $\Delta pH_{50(Mn-Ni)}$ value was found to be 1.96 pH units and the $\Delta pH_{50(Mn-Co)}$ value 2.53 pH units, indicating easy separation of nickel and cobalt from manganese, calcium and magnesium. The extraction and stripping kinetics of cobalt, copper, zinc, and manganese were fast and the extraction and stripping kinetics of nickel were slow with the Versatic 10 acid/LIX® 63 synergistic system. However, the nickel extraction and stripping kinetics significantly increased with the addition of TBP. As a result, the nickel extraction and stripping kinetics are fast enough for industrial operations.

It is proposed that in the Versatic 10 acid/LIX® 63 system, LIX® 63 plays the role of an extractant and Versatic 10 acid a synergist for nickel while LIX® 63 plays the role of a synergist and Versatic 10 acid an extractant for cobalt. This is supported by the difficulty in nickel stripping with both LIX® 63 and LIX® 63/Versatic 10 acid systems, and by the cobalt poisoning

with LIX® 63 system and easy cobalt stripping with the LIX® 63/Versatic 10 acid system in the presence of oxygen. This means that in an organic system containing different reagents, one particular reagent may play a role of an extractant with some metals and a solvating reagent (synergist) with others.

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References

- Cheng, C.Y., 2003. SX applications for nickel and cobalt: pros and cons of existing processes and possible future developments. ALTA SX/IX World Summit, Perth, ALTA Metallurgical Services, Melbourne.
- Cheng, C.Y., Houchin, M., 2001. Solvent extraction process for recovering nickel and cobalt from leach solutions. Patent PCT/AU01/01161, 2001.
- Cheng, C.Y., Urbani, M.D., 2003. Purification of laterite leach solutions by direct solvent extraction. In: Kongoli, F., Itagaki, K., Yamauchi, C., Sohn, H.Y. (Eds.), *Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies. Aqueous and Electrochemical Processing*, vol. 3. TMS, Warrendale, pp. 251–265.
- Cheng, C.Y., Urbani, M.D., 2005a. Solvent extraction process for separation cobalt and/or manganese from impurities in leach solutions. Patent Application No PCT/AU2005/000088 and Patent Publication No. WO 2005/073415 A1.
- Cheng, C.Y., Urbani, M.D., 2005b. Solvent extraction process for separation cobalt and/or nickel from impurities in leach solutions. Patent Application No PCT/AU2005/000099 and Patent Publication No. WO 2005/073416 A1.
- Cheng, C.Y., Urbani, M.D., 2005c. The recovery of nickel and cobalt from leach solutions by solvent extraction: process overview, recent research and development. *Proceedings of ISEC 2005. China Academic Journal Electronic Publishing House, Beijing*, pp. 503–526.
- Cheng, C.Y., Urbani, M.D., Houchin, M., 2003. Synergistic solvent extraction and its potential application to nickel and cobalt recovery. In: Young, C., Alfantazi, A., Anderson, C., James, A., Dreisinger, D., Harris, B. (Eds.), *Hydrometallurgy 2003*. TMS, Warrendale, pp. 787–800.
- Cheng, C.Y., Urbani, M.D., Houchin, M., 2004. Manganese separation by solvent extraction in nickel laterite processing. In: Imrie, W.P., Lane, D.M. (Eds.), *International Laterite Nickel Symposium — Charlotte*. TMS, Warrendale, pp. 429–447.
- Cox, M., Flett, D.S., 1971. Study of the synergistic extraction of metals by α hydroxyoxime/carboxylic acid mixtures with the AKUFVB apparatus. *Proceedings of ISEC '71. Society of Chemical Industry, London*, pp. 204–213. Paper 34.
- du Preez, A.C., Preston, J.S., 2004. Separation of nickel and cobalt from calcium, magnesium and manganese by solvent extraction with synergistic mixtures of carboxylic acids. *J. S. Afr. Inst. Min. Metall.* 333–338 (July).
- Flett, D.S., Titmuss, S., 1968. Synergistic effect of LIX® 63 on the extraction of copper and cobalt by naphthenic acid. *J. Inorg. Nucl. Chem.* 31, 2162–2163.
- Flett, D.S., West, D.W., 1971. Extraction of metal ions by LIX® 63/carboxylic acid mixtures. *Proceedings of ISEC '71. Society of Chemical Industry, London*, pp. 214–223. Paper 40.
- Flett, D.S., Cox, M., Heels, J.D., 1974. Extraction of nickel by α hydroxy oxime/lauric acid mixtures. *Proceedings of ISEC '74*, vol. 3. Society of Chemical Industry, London, pp. 2560–2575.
- Preston, J.S., 1975a. Alpha-substituted oxime extractants — I. Extraction of Cu(II), Ni(II), Co(II) and Fe(III) by aliphatic α -hydroxyoximes. *J. Inorg. Nucl. Chem.* 37, 1235–1242.
- Preston, J.S., 1975b. α -substituted oxime extractants — II. Extraction of Cu(II), Ni(II), Co(II) and Fe(III) by aliphatic α -hydroxyoximes and α -dioximes. *J. Inorg. Nucl. Chem.* 37, 2187–2195.
- Preston, J.S., 1983. Non-chelating oximes in the solvent extraction of base metals. *Proceedings of ISEC '83. AIMChE, New York*, pp. 357–358.
- Preston, J.S., du Preez, A.C., 1994. Synergistic effect in the solvent extraction of some divalent metals by mixtures of Versatic 10 acid and pyridinecarboxylate esters. *J. Chem. Technol. Biotechnol.* 61, 159–165.
- Preston, J.S., du Preez, A.C., 2000. Separation of nickel and calcium by solvent extraction using mixtures of carboxylic acids and alkylpyridines. *Hydrometallurgy* 58, 239–250.
- Swanson, R.R., 1965. Liquid–liquid recovery of copper values using α -hydroxy oximes. US patent No 3,224,873.